Differences in isoprene and monoterpene emissions from cold-tolerant eucalypt species grown in the UK

Differences in isoprene and monoterpene emissions from cold-tolerant eucalypt species grown in the UK

Gemma Purser*[1,2], Mathew R. Heal[2], Stella White[1], James I.L. Morison[3], Julia Drewer[1]

[1] UK Centre for Ecology & Hydrology, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK

[2] School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh, EH9 3FJ, UK

[3] Forest Research, Alice Holt Lodge, Farnham, Surrey, GU10 4TT, UK

*Corresponding author

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Abstract

The UK may be required to expand its bioenergy production in order to make a significant contribution towards the delivery of its 'net zero' greenhouse gas emissions target by 2050. However, some trees grown for bioenergy are emitters of volatile organic compounds (VOCs), including isoprene and terpenes, precursors in the formation of tropospheric ozone, an atmospheric pollutant, which require assessment to understand any consequent impacts on air quality. In this initial scoping study, VOC emission rates were quantified under UK climate conditions for the first time from four species of eucalypts suitable for growing as short-rotation forest for bioenergy. An additional previously characterised eucalypt species was included for comparison. Measurements were undertaken using a dynamic chamber sampling system on 2-3 year-old trees grown under ambient conditions. Average emission rates for isoprene, normalised to 30 °C and 1000 μmol m^{-2} s^{-1} PAR, ranged between 1.3 μg C g_{dw}^{-1} h^{-1} to 10 μg C g_{dw}^{-1} h^{-1}. All the eucalypt species measured were categorised as 'medium' isoprene emitters (1–10 μg C g_{dw}^{-1} h^{-1}). Total normalised monoterpene emission

rates were of similar order of magnitude to isoprene or approximately one order of magnitude lower. The composition of the monoterpene emissions differed between the species and major components included eucalyptol, α-pinene, limonene and β-cis-ocimene. The emission rates presented here contribute the first data for further studies to quantify the potential impact on UK atmospheric composition if there were widespread planting of eucalypts in the UK for bioenergy purposes.

1. Introduction

A number of volatile organic compounds (VOCs), particularly isoprene, monoterpenes and monoterpenoids, classified collectively here as terpenes, are trace gas secondary metabolites that can be emitted from vegetation. It has been suggested that these biogenic VOCs may provide a form of regulation against heat stress (Sharkey et al., 2008), communication and can act as a defence mechanism against disease and predation (Niinemets and Monson, 2013). Terpenes are highly reactive compounds whose oxidation in the lower atmosphere can lead to the formation of secondary organic aerosols (SOA) and, in the presence of nitrogen monoxide (NO), to the production of ozone (O_3). Terpene composition has been found to be an important factor in the magnitude of ozone production (Bonn et al., 2017). Both SOA and O_3 have climate impacts: SOA acts as cloud condensation nuclei (Wang et al., 2016) and tropospheric O_3 is a greenhouse gas (UNEP/WMO, 2011). They both also have detrimental effects on human health, the SOA risk arising because it is a component of fine particulate matter ($PM_{2.5}$) (WHO, 2013). In addition, O_3 causes plant damage (Felzer et al., 2007) leading to reduced agricultural crop yields (Wilkinson et al., 2012). In regions of high NO emissions relative to VOC emissions, such as the UK, VOCs are normally the limiting factor in O_3 formation (Finlayson-Pitts and Pitts, 1993). Experimentally-derived VOC emission rates from different types of vegetation are important for the estimation of tropospheric O_3 concentration in regional air quality models.

Eucalyptus, a tree genus native to predominately mainland Australia and Tasmania, is a known emitter of VOCs. Some eucalypt species, mainly from Tasmania (and some mountainous regions of south-east Australia), are able to tolerate and grow well in colder climates (Williams and Potts, 1996). These species have been the recent focus of assessment and development for bioenergy trials within the UK (Leslie et al., 2019, 2012; Purse and Leslie, 2016; Purse and Richardson, 2001; Stokes, 2015). The UK is required to increase its bioenergy contribution to renewable resources of energy in the future in order to meet the 2050 net zero greenhouse gas emissions target (Committee on Climate Change, 2019) which has now been adopted in UK law. Solutions to increase bioenergy production could include planting of short-rotation forest (SRF) and short-rotation coppice (SRC) eucalypts.

SRF uses single stem trees, as in a conventional forest plantation, but planted at a higher density with a 10 – 20 year rotation (the age at which the trees will be harvested). SRC are usually multi-stem trees; the above ground biomass is harvested on a rotation of 2-5 years and new biomass grows from the rootstock which remains in the ground. The plantation only needs replanting after 20-30 years (Drewer et al., 2018). Both SRF and SRC produce a fast-growing supply of biomass for technologies such as bioenergy with carbon capture and storage (BECCS) but their expansion could lead to changes in VOC emissions across the UK and subsequent changes in air quality, dependant on the species grown. Eucalypts, can be grown as SRF or SRC depending on the growth habit of individual species, with likely rotation of <10 years (Purse and Richardson, 2001). Height growth rates for *E. gunnii* in the UK have been shown to be between 1-2 m per year (Leslie et al., 2018).

However, there is still substantial uncertainty regarding the magnitude and variability of VOC emissions across eucalypt species, including the profile of compounds emitted. Only a few of the approximately 800 species of eucalypts (Coppen, 2002) have had their natural VOC emissions to the atmosphere investigated. In addition, the majority of studies have been

conducted with trees acclimatised to warmer and sunnier climates than found in the UK (Emmerson et al., 2020; Evans et al., 1982; He et al., 2000a; Sørensen et al., 2020; Street et al., 1997; Winters et al., 2009); VOC emission rates for cold tolerant eucalypt species suitable for growing in the UK have not been measured. Hence more data are needed to subsequently determine whether extensive planting of SRF eucalypts will contribute significantly to VOC emissions across the UK and to consequent changes in air quality (Drewer et al., 2018).

VOCs reported as being emitted from eucalypts include isoprene and a range of monoterpenes and functionalised monoterpenes (i.e. monoterpenoids), for example: α-pinene, β-pinene, eucalyptol, limonene, cis-ocimene, terpineol, p-cymene, α-phellandrene and β- phellandrene (Aylott et al., 2008; Franich, 1985; Guenther et al., 1991; He et al., 2000a; King et al., 2006; Owen and Peñuelas, 2013; Rasmussen, 1972; Street et al., 1997; Winters et al., 2009). Both light and temperature can affect the emission rates of isoprene and monoterpenes from leaves of eucalypts (Guenther et al., 1991). The production of terpenes is linked to the activity of isoprene synthase and terpene synthase enzymes which are themselves linked to primary metabolic processes such as photosynthesis (Niinemets, 2015). However, previous studies have found variation in the total emission rates of isoprene and monoterpenes between different species of eucalypt and the relative percentages of the types of monoterpenes emitted (He et al., 2000a, 2000b; Owen and Peñuelas, 2013; Winters et al., 2009). Ratios of monoterpenes in the leaf may be influenced by environmental factors such as temperature, seasonality and herbivory, in addition to genetic variation (Keszei et al., 2008). Therefore, individual measurements of each species under specific growth conditions representative of a particular region are required to determine appropriate VOC emission rates for country specific assessments. In addition, although within-leaf monoterpene concentrations from whole leaf extractions of oil glands reported previously (Li et al., 1996) may be used to provide a qualitative assessment of the types of monoterpenes

emitted by different eucalypt species they may not be able to give an indication of the natural emission rates for some terpenes due to the plant generating “de novo” terpenes, that are emitted directly into the atmosphere shortly after the point of synthesis (Ghirardo et al., 2010). It is well known that emissions of VOCs can vary by orders of magnitude between species, so the intention here was to investigate these relative magnitudes. This scoping study aimed to quantify VOC emission rates of four previously unmeasured eucalypt species potentially suitable for UK bioenergy SRF or SRC and categorise them according to previous literature (Evans et al., 1982; He et al., 2000a) as “low”, “medium” or “high” emitters for isoprene and monoterpenes to help focus future assessment of the impact of any of eucalypt planting on UK air quality.

2. Materials and Methods

2.1 Plant specimens and growing conditions

Two trees of five different species of immature pot-grown eucalypts (aged 2-3 years) were sourced from a specialist UK-based eucalypt grower (hardy-eucalyptus.com, Grafton Nursery, Worcester, UK). The selected species were *E. pauciflora subsp. debeuzevillei, E. johnstonii, E. cordata subsp. quadrangulosa, E. subcrenulata* and *E. globulus subsp. bicostata*. Additionally, emissions from individual trees of a further four UK climate tolerant eucalypt species were also measured during this study. These data are available in the Supplementary Information (SI) but do not form part of the discussion presented here (Table S1).

The trees were initially grown from seed in specialist air-pots® (Caledonian Tree Co. Ltd, Scotland) to promote continued growth of the roots. The 5 L pots were watered daily, and the trees fed weekly with chempak number 4©, high potash feed in accordance to the grower’s recommendations. The trees were acclimatised outdoors for one year at the UK Centre for Ecology & Hydrology (UKCEH), near Penicuik, Scotland (55° 49’ 33.6’ N, 3° 13’

12' W) prior to conducting the measurements. Trees were sampled for either 4 or 5 dry days between June and August 2019 typically during the afternoons between 12 am and 6 pm. Sampling days are given in the SI Table S2. Based on long-term hourly site monitoring data collected at UK CEH the average midday air temperature in June, July and August 2019 was 11.8, 16.0 and 14.5 ºC, respectively. Average midday photosynthetically-active radiation (PAR) was 413, 364 and 346 µmol m^{-2} s^{-1}, for June, July and August. The majority (70%) of the samples were collected in August. Table 1 shows the range of air temperature and PAR during sample collection. Given that both air temperature and PAR are highest during June to August (see SI Figure S1) it is reasonable to assume that VOC emission rates are likely to peak at this time of year for this locality.

2.2 Chamber sampling method

A polyethylene terephthalate (PET) bag (Roast-in-oven bags, Lakeland, Windermere, UK) with a transmissivity of 90% and dimensions 33 x 43 cm (approximately 6 L volume) was gently attached around the stem of a small branch of similar aged leaves along with a temperature and relative humidity probe (CS215, Campbell scientific, Shepshed, UK) and two PTFE tubing lines, one for the inflow of ambient air and one for chamber air sampling (Ortega et al., 2008; Stewart-Jones and Poppy, 2006; Vedel-Petersen et al., 2015). Only leaves fully exposed to the sun were sampled. Temperature and relative humidity were sampled inside the bag every minute. An opening was made at one corner of the bag to allow a steady flow of ambient air through the bag and was smaller in diameter than the inflow line (Sørensen et al., 2020). The air flow was delivered from an oil-free double-ended diaphragm pump (Capex V2, Charles Austen pumps ltd, Surrey, UK) (Morrison et al., 2016) through PTFE tubing at a flow rate between 2-5 L min^{-1}. The air volume was therefore replaced approximately every 1.2-3 min, comparable to previous studies (He et al., 2000a; Winters et al., 2009). The bag was flushed for up to 15 min prior to sample collection. A slight over-pressure of ambient air allowed the sample bags to become inflated, preventing

the foliage from rubbing against the sides of the bag (Ortega et al., 2008; Sørensen et al., 2020). No filter was used on the ambient air supply during sample collection, so information for local average ozone concentrations monitored nearby are provided in SI Table S3 to indicate the conditions under which the branch chamber measurements were conducted. The hourly ozone concentration from the nearby monitoring station ranged from 48-117 μg m^{-3} across the sample days. Whilst it is possible that some ozone entering the chamber may have been lost to the chamber walls (Janson, 1993), it is also possible that the ozone reacted with VOCs emitted from the eucalyptus branches prior to sample collection thereby reducing measured emission rates. As such these emission rates should be considered to be lower estimates of emission rates for eucalyptus species grown and measured under typical UK field conditions.

The PTFE sample line exiting the bag was attached to a hand pump (210-1003MTX, SKC ltd, Blandford Forum, UK) drawing air from inside the bag at a flow rate of 200 mL min^{-1} through a 6 mm OD stainless steel automated thermal desorption (ATD) tube (PerkinElmer, Waltham, MA, USA) packed with 200 mg Tenax TA 60/80 (11982 SUPELCO, Sigma-Aldrich, St Louis, MO, USA) and 100 mg Carbotrap 20/40 (20273 SUPELCO, Sigma-Aldrich). Ambient air outside the bag and air from inside the bag were sampled concurrently for about 30 min resulting in a 6 L sample. Three sequential samples were collected over a 1.5 h period per sampling day. The sample tubes were stored in a fridge at 4 °C prior to analysis.

Measurements of PAR (SKP 215 PAR Quantum Sensor, Skye instruments, Llandrindod Wells, UK) were made at 1-min intervals adjacent to the trees during the sampling but was also separately archived hourly, along with ambient temperature, by a meteorological station at UKCEH. PAR measurements taking outside of the chamber were corrected for a 90% transmissivity of the chamber material to give PAR values appropriate to internal chamber conditions.

2.3 Analytical method

The VOCs collected on the sorbent were analysed using gas chromatography-mass spectrometry (GC-MS) with a two-stage automatic thermal desorption unit (ATD 400, Perkin-Elmer, Wellesley, MA, USA). The samples were desorbed at 280 °C for 6 min under a flow of helium and were subsequently trapped onto a Tenax TA cold trap at 30 °C. The second stage of desorption was achieved by flash heating the cold trap to 300 °C for 6 min to flush the sample through a heated transfer line (200 °C) onto the GC column (Ultra-2 column, 100 m length, 0.2 mm I.D., 5% phenylmethyl silica, Agilent, Palo Alto, CA, USA). The oven was held at 35 °C for 2 min, ramped to 160 °C at 3 °C min^{-1} and then to 280 °C at 45 °C min^{-1} before being held at 280 °C for 10 min (as used in Morrison et al., 2016). Eluting compounds were detected using a tuned Perkin Elmer mass spectrometer (Clarus 500, Perkin Elmer, Wellesley, MA, USA) operating in total ion count mode.

2.4 Calibration

Standards were measured at the start and end of each GC-MS sample run. Isoprene standards were prepared by direct sampling onto a sorbent tube from a certified 700 ppbv gas standard (BOC, UK) for 10, 30, 45 and 60 s using a sample pump (210-1003MTX, SKC ltd, Blandford Forum, UK) producing standards of 65, 198, 296 and 395 ng. Standards (from Sigma-Aldrich, Gillingham, UK) of the monoterpenes α-pinene, β-pinene, limonene, α-phellandrene, β-phellandrene, 3-carene, camphene, γ-terpinene and β-myrcene, and the monoterpenoids (monoterpene-based compounds with, for example, additional oxygen or missing a methyl group) eucalyptol and linalool were prepared as a mixed stock solution of 3 ng μL^{-1} in methanol. (The term monoterpene is used henceforth in this paper to refer to all measured compounds based on the C10 monoterpene formula.)

Aliquots of 1, 2, 3 and 4 µL of the mixed monoterpene stock solution were pipetted directly onto sample tubes under a flow of helium to produce a range of mixed monoterpene standards of 3, 6, 9 and 12 ng. Note that mass loadings of isoprene and monoterpene calibration standards were prepared to greater precision than quoted above but are shown here as nominal values for ease of discussion. Unknown peaks in sample chromatograms were identified by comparison to the internal library of the GC-MS (National Institute of Standards and Technology) and by comparison with the retention time of the standard. Peak areas were used in analyte quantification calculations. No calibration standard was available for β-cis-ocimene, so this was analysed semi-quantitatively using the peak area ratio for the identified β-cis ocimene peak against α-pinene and then multiplied by the mass of α-pinene to give an estimate of the mass of β-cis ocimene collected on the sample tube.

The limit of detection (LoD) for each analyte was calculated using repeated blank measurements to initially calculate the limit of the blank (LoB) for each analyte and then using this with the standard deviation of repeats of the lowest standard concentration for each analyte (isoprene nominal 65 ng and monoterpenes nominal 3 ng) to give an LoD for the analytical method as a mass (ng) (Armbruster and Pry, 2008). Calculated LoDs were as follows: isoprene (21 ng), α-pinene (0.78 ng), β-pinene (0.90 ng), β-phellandrene (0.91 ng), β-myrcene (1.00 ng), α-phellandrene (1.06 ng), limonene (0.60 ng), γ-terpiene (103 ng), 3-carene (0.94 ng), eucalyptol (1.76 ng), camphene (0.92 ng) and linalool (113 ng). In some instances, very low emission rates of a VOC from the eucalypt branch may have resulted in the mass (ng) of VOC collected being less than the respective LoD. During this study, 75% of the samples measured for isoprene were greater than the LoD, although only 4% of those measured for camphene. An example of an emission rate LoD based on the analytical LoD (ng) is 0.16 µg C gdw^{-1} h^{-1} (16 µg C m^{-2} h^{-1}) for isoprene and for monoterpenes (limonene and eucalyptol respectively) in the range of 0.0045-0.013 µg C gdw^{-1} h^{-1} (0.45-1.3 µg C m^{-2} h^{-1}) assuming the following parameters: 30 min subsample at a flow rate of 200 mL min^{-1}

from a chamber containing a nominal total leaf mass of 4 g or total leaf area of 0.04 m^2 with a chamber flow rate of 3 L min^{-1}.

2.5 Calculation of VOC emission rates

Subsequent to VOC sampling, the leaves of each branch were collected and scanned using a LI-3100c area meter (LI-Cor Inc, Lincoln, NE, USA) to give single-sided leaf surface area (m^2). The leaves were then weighed prior to and after drying to constant mass in an oven at 70 °C for 48 h. This permitted VOC net foliage emission rate (ER) to be expressed on either a leaf area, A, basis (μg C m^{-2} h^{-1}), or a leaf dry mass, m_{dry}, basis (μg C g_{dw}^{-1} h^{-1}), according to Equations 1 and 2.

Equation 1 $$Leaf\ mass\ ER = \frac{[C_{out} - C_{in}] \times Q}{m_{dry}}$$

Equation 2 $$Leaf\ area\ ER = \frac{[C_{out} - C_{in}] \times Q}{A}$$

In these equations, Q is the flow rate of ambient air through the chamber and C_{out} and C_{in} are the concentrations of VOC (μg L^{-1}) collected on the sorbent tubes for the ambient air and chamber samples, respectively, with VOC mass scaled to per hour equivalent and expressed as the VOC carbon content.

Average chamber temperature and PAR were measured for the duration of each individual 30 min sample. Both PAR and temperature are known to influence the emission rates of isoprene (Guenther et al., 1993) and so all isoprene measurements were normalised to 1000 μmol m^{-2} s^{-1} PAR and 30 °C. It is acknowledged that emissions of some monoterpenes, such as, α-pinene, may also be produced during de novo synthesis with their emission rates changing in response to fluctuations in PAR (Ghirardo et al., 2010). However, eucalypt leaves contain numerous sub-dermal secretory cavities, referred to here as oil storage glands, which have been shown to contain largely monoterpenes and are likely the dominant source of monoterpene emissions. Therefore, emissions of all monoterpene compounds are in this instance only normalised for temperature (30 °C) in accordance with the algorithm

developed by Guenther et al. (1993). The normalised emission rates for each sample were then averaged (including instances of samples with no apparent emission rate or only trace emission rate) to produce a single emission rate per species (Table 1). The average uncertainties for a calculated emission rate was 16% for isoprene and 17% for monoterpene emissions which were derived from the uncertainty in the following measured and calculated parameters: interpolation from the relevant calibration regression fit; sample time; chamber volume; chamber flow rate; sample pump flow rate, foliage dry mass or leaf area; temperature; PAR. The error propagation equation and the error assigned to each parameter is described in Supplementary Information Section S1.

3. Results and discussion

3.1 Isoprene emissions

Isoprene was emitted by all five eucalypt species and the average normalised emission rate for each species measured in this study is shown in Figure 1. The number and ranges of emission rates, together with the ranges of PAR, chamber temperature and humidity across the sampling periods, are presented in Table 1.

The species with the largest isoprene emission based on leaf mass was *E. globulus subsp. Bicostata*, averaging 10.1 μg C g_{dw}^{-1} h^{-1} (704 μg C m^{-2} h^{-1}), and based on leaf area was *E.subcrenulata*, averaging 1136 μg C m^{-2} h^{-1} (6.16 μg C g_{dw}^{-1} h^{-1}). The lowest average emission rate was about an order of magnitude less, from *E. pauciflora subsp. debeuzevillei* at 1.31 μg C g_{dw}^{-1} h^{-1} (183 μg C m^{-2} h^{-1}). Eucalypts have been generically categorised as high emitters of isoprene (i.e. ER > 10 μg C g_{dw}^{-1} h^{-1}), with previous reported measurements being in the range 10-33 μg C g_{dw}^{-1} h^{-1} (Evans et al., 1982).

However, in this study all the eucalypt species studied are categorised as medium emitters, with emission rates between 1-10 μg C g_{dw}^{-1} h^{-1}. Although *E. globulus* gave an emission rate

298 of 10.1 μg C g_{dw}^{-1} h^{-1} this is not deemed significantly greater than 10 to classify it in the high
299 emitter category.
300
301
302 PAR fluctuated across the sampling campaign depending on the time of day, day of the year
303 and local cloud cover, and, consistent with previous literature (Guenther et al., 1991; He et
304 al., 2000a; Winters et al., 2009), isoprene emission rates were generally observed to
305 increase with increasing PAR although the relationship between isoprene emissions and
306 PAR for some species was less clear. Figure 2 shows an example for *E. subcrenulata*. It is
307 noted that two measurement for PAR between 400 - 700 μmol m^{-2} s^{-1} measured on the same
308 day seem to be outliers, the reasons for which are unclear. The remaining data exhibit a
309 significant relationship between isoprene and PAR (R^2 = 0.47, P = 0.01).
310
311 ### 3.3 Isoprene emission comparisons with other studies
312 This study reports the first investigation into the isoprene emission rates for *E. pauciflora*
313 *subsp. debeuzevillei, E. johnstonii, E. cordata subsp. quadrangulosa,* and *E. subcrenulata*,
314 so no direct comparisons to literature values are possible. However, emission rates from *E.*
315 *globulus* have been reported previously, as summarised in Table 2, so can serve as a guide
316 on the validity of the measurements in this study for the previously untested species. It is
317 worth noting, however, that the subspecies of *E. globulus* measured in previous studies is
318 not documented and different subspecies may well have different emission rates. The *E.*
319 *globulus subsp. bicostata* subspecies investigated here is a more cold-tolerant subspecies
320 and the seed provenance from which they are grown will reflect this, which in turn could
321 produce genetic compositions that yield differing VOCs. This has been noted for
322 monoterpene composition (Boland et al., 1982).
323

The average emission rate for *E. globulus subsp. bicostata* measured in this study was lower than those reported by Evans et al. (1982) and He et al. (2000a) when compared on a dry leaf mass basis (Table 2). These earlier studies were conducted on trees that likely experienced much warmer growing conditions. However, the emission rates reported here are of the same order of magnitude as those from measurements conducted on mature foliage during a field campaign in Australia in which cool and cloudy weather was reported (Winters et al., 2009). These latter sampling conditions would be closer to those encountered in Scotland when the measurements in the present study were made. The temperature at which plants develop, in addition to the temperature and light conditions in the days prior to leaf sampling, have been found to influence emission rates of isoprene due to the regulation of the enzyme, isoprene synthase and the production of dimethylallyl diphosphate (DMADP), the substrate required for isoprene production (Monson et al., 1992; Sharkey et al., 2008). This may explain to some degree the lower isoprene emission rates for *E. globulus subsp. bicostata* measured during the present study. In direct sunlight on hot days the temperatures inside the chamber during sample collections were higher than ambient temperatures (by between 2 and 9 ºC) which is a common effect of using this type of methodology to collect VOC emissions (He et al., 2000a; Ortega and Helmig, 2008) and low flow rates for chamber flushing – but on no occasion did chamber temperature exceed the critical threshold of 38 °C, above which enzyme deactivation occurs and a decline in isoprene emission from *E. globulus* has been reported (Guenther et al., 1991). It is also worth noting that the isoprene emissions from *E. globulus subsp. bicostata* measured in this study were within the range of isoprene emission rates reported for a UK-based greenhouse study (with artificially enhanced light conditions) (Owen and Peñuelas, 2013) (Table 2).

It has been suggested that levels of the isoprene synthase enzyme that regulates isoprene emissions can be lower in immature leaves of some species (Vickers et al., 2010). In this regard, the emissions from the new immature foliage of *E. globulus subsp. bicostata* on a leaf area basis compared very well with similar immature foliage (<15 days old) at standard

conditions reported by Guenther et al. (1991) and on a leaf mass basis with the young leaves of reported by Street et al (1997) (Table 2). This type of immature, young and rapidly expanding foliage is highly representative of the first few years of eucalypt plantations that are managed as short-rotation coppice. In these situations, the multi stemmed trees can grow up to 2 m per year (Leslie et al., 2018).

3.4 Total monoterpene emissions

Average total normalised monoterpene emission rates were generally low across all five eucalypt species (Figure 1 and Table 1). Total monoterpene emission rates varied from 0.304 μg C g_{dw}^{-1} h^{-1} (52.6 μg C m^{-2} h^{-1}) for *E. jonstonii* to 1.73 μg C g_{dw}^{-1} h^{-1} (302 μg C m^{-2} h^{-1}) for *E. cordata subsp. quadrangulosa*, except for *E. globulus bicostata* which had an almost 10-fold higher emission rate of 14.1 μg C g_{dw}^{-1} h^{-1} (949 μg C m^{-2} h^{-1}). It was noted that the highest emitting monoterpene species, *E. globulus subsp. bicostata* and *E. cordata subsp. quadrangulosa*, had much softer new-growth foliage and waxier leaves than the other species which often produced thicker sturdier leaves. Total normalised monoterpene emission rates are generally the same or one order of magnitude lower than normalised emission rates measured for isoprene (Table 1), which has been reported in previous eucalypt studies (Emmerson et al., 2016; He et al., 2000a).

Emission rates of monoterpenes from leaves are known to be driven by the monoterpene vapour pressure, which is dependent on compound volatility, oil gland concentration and air temperature (Lerdau et al., 1997). In addition, it is well known that monoterpene emission rates increase with temperature (Emmerson et al., 2020; Guenther et al., 1991; He et al., 2000a; Nunes and Pio, 2001; Street et al., 1997; Tingey et al., 1980). During this study, temperature associations with monoterpene emissions were observed for some of the species such as *E. pauciflora subsp. debeuzevillei* (Figure 3), although given the similar temperatures at which daily measurements were conducted this was not always obvious in

all species. Temperature can also act to regulate the productivity of the terpene synthase enzymes and so alter the concentration of monoterpene found in the leaf glands, which will have an impact upon leaf emissions. Some monoterpenes such as α-pinene may also be light sensitive and their production via de novo synthesis can be correlated to the level of PAR. During this study however, no clear correlation was observed between monoterpene emissions and PAR which suggests that the monoterpenes may have been directly emitted from the storage glands. It is worth noting that emission rates from any previous field-based studies used as a species comparison here are likely also to be influenced by a range of other environmental factors such as limited availability of water (Bonn et al., 2019) in contrast to the well-watered trees used in the present work.

3.5 Total monoterpene emission comparisons with other studies

This study reports the initial assessment of monoterpene emission rates to the atmosphere for *E. pauciflora subsp. debeuzevillei*, *E. johnstonii*, *E. cordata subsp. quadrangulosa*, and *E. subcrenulata* so no direct comparisons to literature values are possible. A comparison of the emission rates from *E. globulus subsp. bicostata* from this study with previous literature is presented in Table 2.

The monoterpene emissions from *E. globulus subsp. bicostata* reported in this study are comparable to those reported by He et al. (2000a) but are three times lower than those reported for the same species by Winters et al. (2009). The monoterpene emissions measured from *E. globulus subsp. bicostata* in this study were also within the range reported by one other UK study (Owen and Peñuelas, 2013), though these latter emission rates were not normalised to standard conditions. It has been suggested that monoterpene emissions from experiments on eucalypts may arise initially via a process of leaf damage to the subcuticular glands rather than an active release process (Guidolotti et al., 2019). However, this suggestion does not fully explain the similar monoterpene emission rates (for a given

406 species) observed across studies, including this one, that have been measured in different
407 locations and under a range of experimental conditions.
408
409 ### 3.6 Monoterpene composition
410 All five eucalypt species emitted similar monoterpenes but the relative proportions of these
411 compounds varied across species as is evident in Figure 4. The major monoterpenes
412 emitted from all five eucalypts were eucalyptol, β-cis-ocimene, α-pinene and limonene
413 (Table 1 and Figure 4). The compounds β-pinene, β-myrcene, α-phellandrene, β-
414 phellandrene and 3-carene were also quantified (Table 1). Small amounts of other
415 monoterpenes were found in the samples but were not positively identified or quantified as
416 they were not part of the calibration and proportionally not important.
417
418 Monoterpene emissions from *E. globulus subsp. bicostata* were dominated by eucalyptol,
419 accounting for 60% of the total monoterpene emissions. Other species such as *E.*
420 *debeuzevillei and E. cordata subsp. quadrangulosa* are both high emitters of β-cis-ocimene
421 while *E. subcrenulata* and *E. johnstonii* emitted roughly similar proportions of eucalyptol, α-
422 pinene and limonene or eucalyptol and α-pinene respectively.
423
424 Monoterpene emissions from *E. globulus* are well represented in literature (Evans et al.,
425 1982; Guenther et al., 1991; He et al., 2000a; Kanagendran et al., 2018; Nunes and Pio,
426 2001; Owen and Peñuelas, 2013; Rasmussen, 1972; Street et al., 1997; Winters et al.,
427 2009). The emissions of eucalyptol, the predominant emitted monoterpene found for *E.*
428 *globulus* in this study, compared well with those from new foliage (<15 days old) reported by
429 Guenther et al. (1991). However, *E. globulus* has previously been reported to be a major α-
430 pinene emitter (Guenther et al., 1991), whereas here it was observed to be a predominantly
431 eucalyptol emitter. Intrinsic natural variation between individuals of the same species is a
432 possible explanation. The chemical variation of monoterpenes found in the oil-bearing

glands of some eucalypt species has been linked to the genetic variation within the genus (Borzak et al., 2015; Keszei et al., 2010; Külheim et al., 2015; Padovan et al., 2017, 2012; Shepherd et al., 1999). In some instances, different chemotypes of a species may arise, with some individuals of the same species having emissions dominant in different percentages of monoterpenes (Bäck et al., 2012; Brophy and Boland, 1990; Kännaste et al., 2013).

For the other four species in this study it is not possible to compare the natural monoterpene emission proportions with any previous study although data for the range of compounds extracted from the glandular cells in the leaves have been reported for *E. subcrenulata, E. cordata, E. johnstonii* and *E. globulus* (Bignell et al., 1998; Li et al., 1996, 1995). No data on the composition of the oils from *E. pauciflor*a subsp. deubuzevelli could be found in the literature. The leaf gland extractions were dominated by eucalyptol for all four species of eucalypt, followed by α-pinene, limonene and then γ-terpinene. In this study, all species were found to have major emissions of eucalyptol, α-pinene and limonene but γ-terpinene was only found in trace amounts. Only *E.globulus* was found to be a major eucalyptol emitter which is comparable to the findings of Li et al (1996). The other emitted species were dominated by α-pinene, limonene or β-cis-ocimene, all compounds which can be produced by de novo synthesis and so could explain to some degree the lack of these compounds found in the storage glands of the previous study. It is worth noting that the emissions composition data in the present study is only comparable qualitatively to the previous oil gland composition data. Different species chemotypes may also exist and would require further investigation with many more tree replicates grown from a range of seed provenances. However, a study by Sørensen et al. (2020) in which atmospheric emissions of monoterpenes from eucalypts were compared directly to their extracted leaf oil monoterpene concentrations from the storage glands also reported that no such correlation could be inferred.

3.7 Natural variation of emission measurements

VOC emission rates varied widely between individual trees, as reflected by the standard deviation, minimum and maximum values in Table 1. Using the example of *E. subcrenulata*, the variability (expressed as standard deviation) of isoprene and total monoterpenes for sequential measurements collected on the same day on the same branch were 33% and 35% respectively. Emission rate variability for samples collected between two individuals of the same species on the same day was slightly higher, isoprene (43%) and monoterpenes (38%), compared to the within day variability. The variability for monoterpene emissions between two individuals of the same species, collected using different branches across different sample days was similar (31%) compared to the within day and between species measured on the same day. Isoprene emission variability, however, was slightly higher at 53%. The variability observed in the present branch study is similar in some cases to that of leaf variability reported by Guenther et al. (1991), where the day-to-day emission variability of isoprene (14%) and monoterpenes (>50%) were much lower than the leaf-to-leaf emission rate of isoprene (62%) and monoterpenes (80%). The higher variability for isoprene found during this branch study compared to the previously reported leaf study (Guenther et al., 1991) for the same within day serial sampling could be due to the unavoidable shading of some leaves within the branch chamber. Other studies have also reported similar large variability in emission rates up to 80% for isoprene and 60% for total monoterpenes (He et al., 2000a).

4. Trends in eucalypts for bioenergy

Knowledge of the suitability of certain eucalypt species for bioenergy plantations in the UK is evolving. Sales figures for eucalypt seedlings and saplings in the UK show that *E. glaucescens* accounted for 40% of the 220,000 cell-grown plants sold during the 5-year period 2011-2015 (Purse and Leslie, 2016). However, a more recent poll of species produced and sold as plugs in 2019 could suggest that other species such as *E. rodwayi* and

E. dalrympleana are also gaining popularity (personal comment from the eucalypt seedling growers).

The choice of species is dictated by soil type and local climate conditions, in particular rainfall, minimum temperatures and number of frost days (Leslie et al., 2012; Purse and Leslie, 2016) therefore, different species may be grown as bioenergy plantations in different regions of the UK. With climate warming the geographical ranges over which species may be planted is likely to change. In 2018, 94,000 hectares of land in the UK were used to grow bioenergy crops (Defra, 2019). Bioenergy in the UK has to date focused mostly on two main crops, willow, grown as short-rotation coppice and *Miscanthus*, a perennial grass, harvested annually. Eucalypts produce higher yields of biomass per hectare than willow or *Miscanthus*, making them potentially more desirable as a future crop for bioenergy (Scottish Forestry, 2020).

The measurements on eucalypt species relevant for UK climate conditions presented in this paper are the initial steps required to assess the impacts of VOC emissions from bioenergy plantations. The data reported here only account for emissions from young living leaves on trees; other sources of VOC emissions from a bioenergy plantations may exist such as those from leaf litter, stems and harvesting practices. Further work on plantation scale emissions is needed to fully understand the contribution of VOCs from a range of sources within SRF and SRC plantations. Also, the eucalypt species measured here produced isoprene and monoterpene emissions of varying amounts. In some cases isoprene and monoterpene emissions were equal and in others there was at least an order of magnitude difference in these emission rates. Given the complex air chemistry that may arise under such circumstances, such as the formation of ozone and SOA (Bonn et al., 2017), it is important that atmospheric models are used to assess the potential changes that VOC emissions from eucalypt bioenergy forests grown for the purposes of reducing CO_2 emissions may have on air quality in the UK.

5. Conclusions

Isoprene and monoterpene emission rates were quantified for the first time under UK climate conditions from four species of eucalypt suitable for growing as short-rotation forest or coppice for bioenergy, and from a previously measured eucalypt species as a point of reference. All eucalypt species could be classified as 'medium' isoprene emitters with a normalised emission rate between 1-10 μg C g_{dw}^{-1} h^{-1}. Total monoterpene emissions rates were approximately one order of magnitude lower or similar to those of isoprene. A natural variation in emission rates between different eucalypt saplings and different branches was noted. The composition of the total monoterpene emissions differed between the species of eucalypt, but all included eucalyptol, α-pinene, β-cis-ocimene and limonene as their major monoterpenes. *E. globulus subsp. bicostata was a* major eucalyptol emitter, accounting for around 60% of quantified total monoterpene. Emissions from two eucalypt species *E. cordata subsp. quadrangulosa* and *E. pauciflora subsp. debeuzevillei* were dominated by β-cis-ocimene (38-44% of total quantified monoterpenes) whilst *E. johnstonii* emitted similar proportions of α-pinene (38%) and eucalyptol (37%). The UK requires future expansion of bioenergy plantations in order to fulfil net zero greenhouse gas emissions targets. The emission rates for VOCs measured here are essential first data for future assessments of biosphere-atmosphere interactions arising from any expansion of eucalypt bioenergy plantations and of their potential impact on UK air quality.

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739 Table 1 – Summary of the range of emission rates of isoprene and selected monoterpenes on a leaf area and leaf dry weight basis for five UK
740 eucalypt species grown and measured under a UK climate. The ranges in values of *T*, PAR and RH across the sampling occasions for each
741 species are also presented.

742

Eucalypt species	*N*	d	*T* / °C	PAR / µmol m^{-2} s^{-1}	RH / %	Compound	Emission rate / µg C g_{dw}^{-1} h^{-1}					Emission rate / µg C m^{-2} h^{-1}				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
E. subcrenulata	14	4	21.5 - 29.3	477 - 1458	72.4 - 81.1	Isoprene	6.16	2.53	2.19	12.3	6.03	1130	523	253	2180	1110
						γ-terpinene	0.00	0.01	0.00	0.02	0.00	0.73	1.06	0.00	0.31	0.27
						Linalool	0.01	0.01	0.00	0.03	0.00	1.59	2.25	0.00	6.65	0.47
						α-pinene	0.06	0.06	0.02	0.22	0.04	11	10.2	2.03	38.7	7.91
						Camphene	0.00	0.00	0.00	0.01	0.00	0.11	0.27	0.00	0.82	0.00
						β-phellandrene	0.03	0.04	0.00	0.12	0.01	5.06	7.16	0.00	20.4	1.19
						β-pinene	0.01	0.01	0.00	0.03	0.00	1.00	1.35	0.06	4.69	0.31
						β-myrcene	0.01	0.01	0.00	0.02	0.00	1.02	1.39	0.00	3.75	0.50
						α-phellandrene	0.00	0.01	0.00	0.02	0.00	0.56	0.97	0.00	2.75	0.00
						3-carene	0.01	0.03	0.00	0.12	0.00	2.44	5.98	0.00	21.3	0.03
						d-limonene	0.09	0.12	0.02	0.42	0.04	15.5	21	1.89	74.4	8.14
						Eucalyptol	0.06	0.06	0.01	0.18	0.03	11.5	11.7	0.98	32.1	6.39
						β-cis-ocimene	0.08	0.07	0.00	0.21	0.08	12.1	9.26	0.47	24.1	12.2
						Total MT	0.35	0.32	0.08	1.26	0.28	62.6	57.8	15.5	223	47.1

743

744 N = Total number of measurements; d = Total number of sampling days, T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard
745 deviation

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749 (Table 1 continued)

Eucalypt species	*N*	d	*T* / °C	PAR / µmol m^{-2} s^{-1}	RH / %	Compound	Emission rate / µg C g_{dw}^{-1} h^{-1}					Emission rate / µg C m^{-2} h^{-1}				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
E. johnstonii	9	4	30.0 - 36.6	1249 – 1107	60.3 - 70.4	*Isoprene*	2.86	2.33	0.05	6.99	2.18	471	359	5.88	1140	369
						γ-terpinene	0.00	0.00	0.00	0.00	0.00	0.12	0.18	0.00	0.42	0.00
						Linalool	0.01	0.01	0.00	0.02	0.00	0.88	1.05	0.00	2.46	0.06
						α-pinene	0.11	0.10	0.00	0.35	0.10	20.0	18.3	0.45	63.7	16.9
						Camphene	0.00	0.00	0.00	0.00	0.00	0.09	0.10	0.00	0.22	0.06
						β-phellandrene	0.01	0.00	0.00	0.01	0.01	0.88	0.83	0.00	2.07	1.08
						β-pinene	0.01	0.01	0.00	0.01	0.00	1.06	1.02	0.04	2.60	0.59
						β-myrcene	0.01	0.01	0.00	0.02	0.00	0.75	0.97	0.00	2.76	0.12
						α-phellandrene	0.00	0.00	0.00	0.01	0.00	0.17	0.45	0.00	1.36	0.00
						3-carene	0.00	0.00	0.00	0.01	0.00	0.44	0.43	0.00	1.20	0.25
						d-limonene	0.04	0.02	0.00	0.07	0.04	7.02	3.91	0.00	13.0	7.22
						Eucalyptol	0.11	0.08	0.00	0.26	0.14	19.2	14.8	0.00	46.8	24.0
						β-cis-ocimene	0.01	0.02	0.00	0.07	0.01	2.06	2.66	0.00	8.26	2.24
						Total MT	0.30	0.19	0.01	0.69	0.32	52.6	33.9	0.89	124	54.5

N = Total number of measurements; d = Total number of sampling days, T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard deviation

(Table 1 continued)

Eucalypt species	*N*	d	*T* / °C	PAR / µmol m^{-2} s^{-1}	RH / %	Compound	Emission rate / µg C g_{dw}^{-1} h^{-1}					Emission rate / µg C m^{-2} h^{-1}				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
E. globulus subsp. bicostata	14	4	24.5 - 36.6	848 – 1064	60.3 - 75.5	*Isoprene*	10.1	6.75	2.36	28.2	9.57	704	487	133	2100	713
						γ-terpinene	0.03	0.04	0.00	0.12	0.02	2.06	2.70	0.00	8.13	0.90
						Linalool	0.24	0.28	0.00	0.86	0.15	16.1	18.7	0.00	57.0	10.3
						α-pinene	2.47	3.17	0.02	10.1	1.59	171	223	1.34	674	102
						Camphene	0.01	0.01	0.00	0.02	0.00	0.40	0.53	0.00	1.61	0.15
						β-phellandrene	0.03	0.03	0.00	0.10	0.02	1.67	1.59	0.00	5.10	1.59
						β-pinene	0.06	0.08	0.00	0.32	0.04	4.34	5.69	0.00	21.2	2.85
						β-myrcene	0.16	0.16	0.00	0.59	0.13	10.9	12.0	0.00	43.9	7.38
						α-phellandrene	0.01	0.02	0.00	0.06	0.01	0.91	1.23	0.00	4.12	0.39
						3-carene	0.01	0.01	0.00	0.02	0.00	0.39	0.45	0.00	1.59	0.23
						d-limonene	1.34	1.87	0.00	6.57	0.66	90.9	129	0.25	437	34.2
						Eucalyptol	8.56	13.6	0.02	52.3	5.29	572	907	1.56	3480	394
						β-cis-ocimene	1.17	1.57	0.00	4.70	0.64	78.7	104	0.12	313	42.0
						Total MT	14.1	19.7	0.04	75.4	7.41	949	1320	3.32	5010	552

N = Total number of measurements; d = Total number of sampling days, T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard deviation

(Table 1 continued)

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Eucalypt species	*N*	d	*T* / °C	PAR / µmol m^{-2} s^{-1}	RH / %	Compound	Emission rate / µg C g_{dw}^{-1} h^{-1}					Emission rate / µg C m^{-2} h^{-1}				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
E. pauciflora subsp. debeuzevillei	23	5	29.6 - 32.3	745- 1336	74.5 - 81.4	*Isoprene*	1.31	1.45	0.06	4.71	0.56	183	190	8.38	671	105
						γ-terpinene	0.01	0.02	0.00	0.06	0.00	1.92	2.59	0.00	7.61	0.67
						Linalool	0.14	0.26	0.00	0.93	0.01	18.0	33.9	0.00	122	1.67
						α-pinene	0.05	0.05	0.00	0.18	0.02	6.36	6.79	0.00	24.0	3.57
						Camphene	0.00	0.00	0.00	0.01	0.00	0.09	0.19	0.00	0.79	0.00
						β-phellandrene	0.03	0.04	0.00	0.15	0.01	3.59	6.08	0.00	20.9	1.19
						β-pinene	0.01	0.01	0.00	0.04	0.00	1.12	1.81	0.00	6.29	0.44
						β-myrcene	0.02	0.02	0.00	0.06	0.01	2.16	2.56	0.00	7.63	1.03
						α-phellandrene	0.01	0.01	0.00	0.02	0.00	0.82	0.75	0.00	2.87	0.59
						3-carene	0.01	0.01	0.00	0.02	0.00	0.96	1.01	0.00	3.24	0.60
						d-limonene	0.06	0.08	0.00	0.30	0.02	7.80	10.1	0.00	39.4	3.83
						Eucalyptol	0.17	0.19	0.00	0.78	0.15	23.2	25.0	0.00	102	18.3
						β-cis-ocimene	0.40	0.79	0.00	2.86	0.02	52.3	102	0.06	376	3.57
						Total MT	0.90	1.36	0.02	4.81	0.28	118	176	3.10	631	42.1

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773 N = Total number of measurements; d = Total number of sampling days, T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity SD = Standard
774 deviation

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780 (Table 1 continued)

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Eucalypt species	*N*	d	*T* / °C	PAR / µmol m^{-2} s^{-1}	RH / %	Compound	Emission rate / µg C g_{dw}^{-1} h^{-1}					Emission rate / µg C m^{-2} h^{-1}				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
E. cordata subsp. quadrangulosa	14	4	19.9 - 31.4	731 - 1867	74.5 - 90.4	*Isoprene*	2.43	1.62	0.17	5.37	1.79	391	239	32.0	791	330
						γ-terpinene	0.01	0.02	0.00	0.06	0.00	1.11	2.39	0.00	9.24	0.57
						Linalool	0.01	0.02	0.00	0.08	0.01	2.50	3.86	0.00	14.4	1.06
						α-pinene	0.36	0.74	0.00	2.80	0.06	62.8	137	0.00	515	10.2
						Camphene	0.00	0.00	0.00	0.01	0.00	0.14	0.33	0.00	1.16	0.00
						β-phellandrene	0.02	0.02	0.00	0.05	0.01	2.74	2.75	0.00	7.42	1.57
						β-pinene	0.01	0.01	0.00	0.02	0.00	0.87	1.09	0.00	3.04	0.26
						β-myrcene	0.01	0.01	0.00	0.03	0.01	2.11	1.54	0.00	6.09	2.03
						α-phellandrene	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.00	0.11	0.00
						3-carene	0.02	0.03	0.00	0.09	0.00	2.61	4.83	0.00	13.1	0.00
						d-limonene	0.15	0.16	0.00	0.41	0.06	23.7	25.2	0.00	76.1	10.7
						Eucalyptol	0.50	0.91	0.00	3.33	0.16	88.2	168	0.00	612	25.9
						β-cis-ocimene	0.66	1.11	0.00	4.13	0.36	115	196	0.00	726	59.6
						Total MT	1.73	2.02	0.00	6.96	0.90	302	370	0.00	1270	144

782

783 N = Total number of measurements; d = Total number of sampling days, T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard
784 deviation

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790 Table 2 – Comparison of isoprene and monoterpene emission rates from *E. globulus* with
791 previous literature values.

	Emission rate per leaf area / μg C m^{-2} h^{-1}				Emission rate per dry leaf mass / μg C g_{dwt}^{-1} h^{-1}					
species	isoprene	total MT	eucalyptol	α-pinene	isoprene	total MT	eucalyptol	α-pinene	Ref	Comment
E. globulus subsp. bicostata	696	949	572	171	10.0	14.1	8.56	2.47		This study
E. globulus					38.5		3.53	1.14	1	A
	562		1250	6430					2	B
	2590		648	2980					2	C
	3750		475	2720					2	D
	7410	871	380	152	68.5	5.41	2.37	0.89	3	E
	443	3310			1.76	13.2			4	E
					3.84	17.1	11.5	2.49	5	A,F
					37.0	185	133	27.3	5	A,G
					14.9	5.30	1.67	1.17	6	E, H
					48.7	0.700	0.00400	0.0890	6	E, I

792 MT = monoterpene. Ref = Literature reference: 1. (Evans et al., 1982) (not normalised); 2. (Guenther et al.,
793 1991); 3. (He et al., 2000a) (normalised to 30 °C and 1000 μmol m^{-2} s^{-1} PAR); 4. (Winters et al., 2009)
794 (normalised to 30 °C and 1000 μmol m^{-2} s^{-1} PAR); 5. (Owen and Peñuelas, 2013) (not normalised); 6. (Street et
795 al. 1997).

796 A. not normalised; B. 28 °C and 1000 μmol m^{-2} s^{-1} PAR, leaf age <15 days converted to μg C g_{dw}^{-1} h^{-1}; C. 28 °C
797 and 1000 μmol m^{-2} s^{-1} PAR, leaf age 15 - 40 days converted to μg C g_{dw}^{-1} h^{-1}; D. 28 °C and 1000 μmol m^{-2} s^{-1} PAR,
798 leaf age 40 + days converted to μg C g_{dw}^{-1} h^{-1}; E. 30 °C and 1000 μmol m^{-2} s^{-1} PAR; F. Minimum reported value
799 converted to μg C g_{dw}^{-1} h^{-1}; G. maximum reported value converted to μg C g_{dw}^{-1} h^{-1}; H. Young leaves; I. Old leaves

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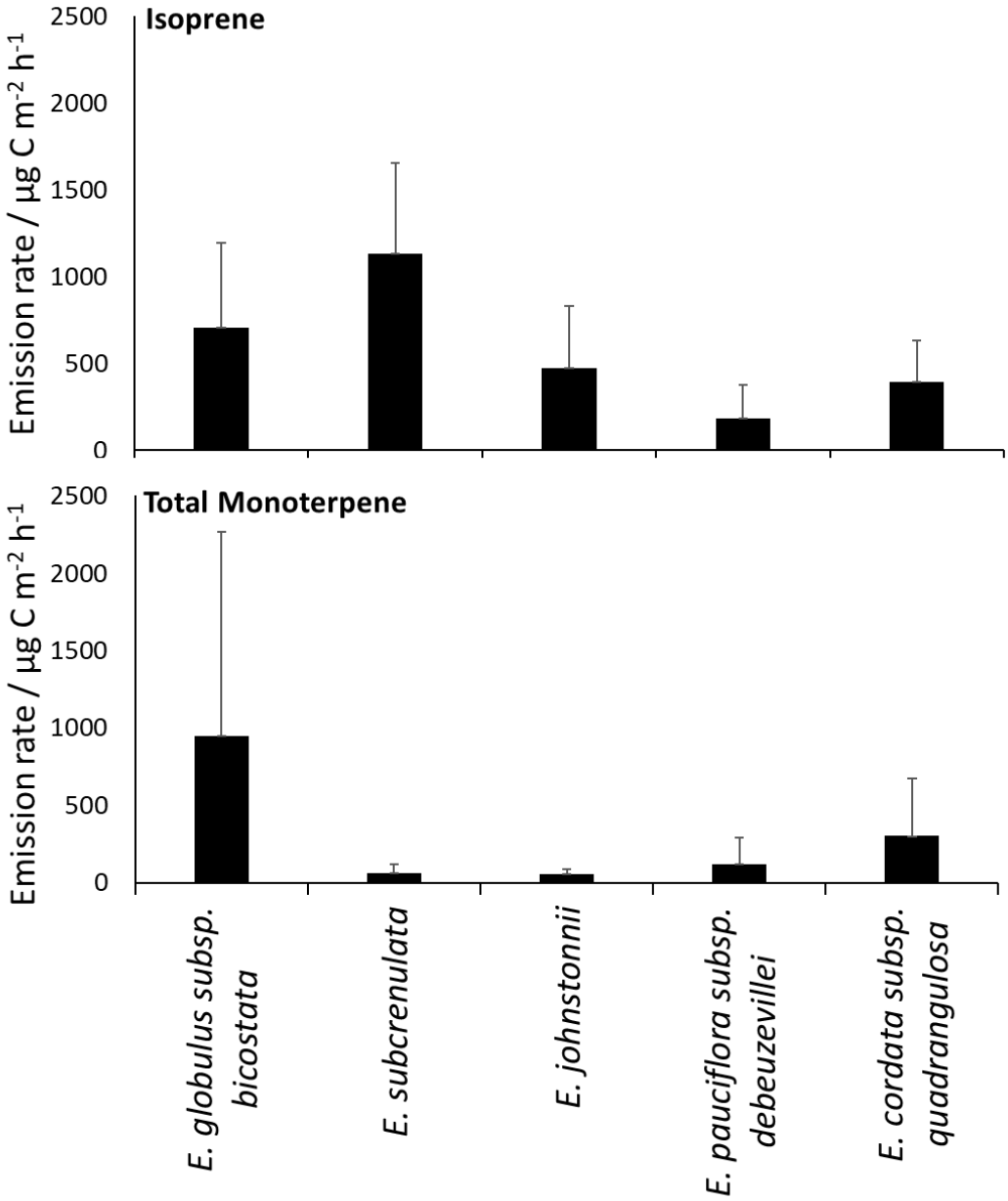

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807 Figure 1 – Average isoprene and total monoterpene emission rates for 5 eucalypt species
808 grown and measured under a UK climate. Emission rates are expressed on a per leaf area
809 basis and are normalised to 1000 µmol m^{-2} s^{-1} PAR and 30 °C for isoprene and to 30 °C for
810 monoterpenes using the algorithm of Guenther et al. (1993). The error bars show the
811 standard deviation for the total measurements for each species and the numbers of
812 measurements contributing to each average emission rate are given in parentheses. The
813 isoprene and total monoterpene data are presented on the same scale to illustrate their
814 relative emission rates.

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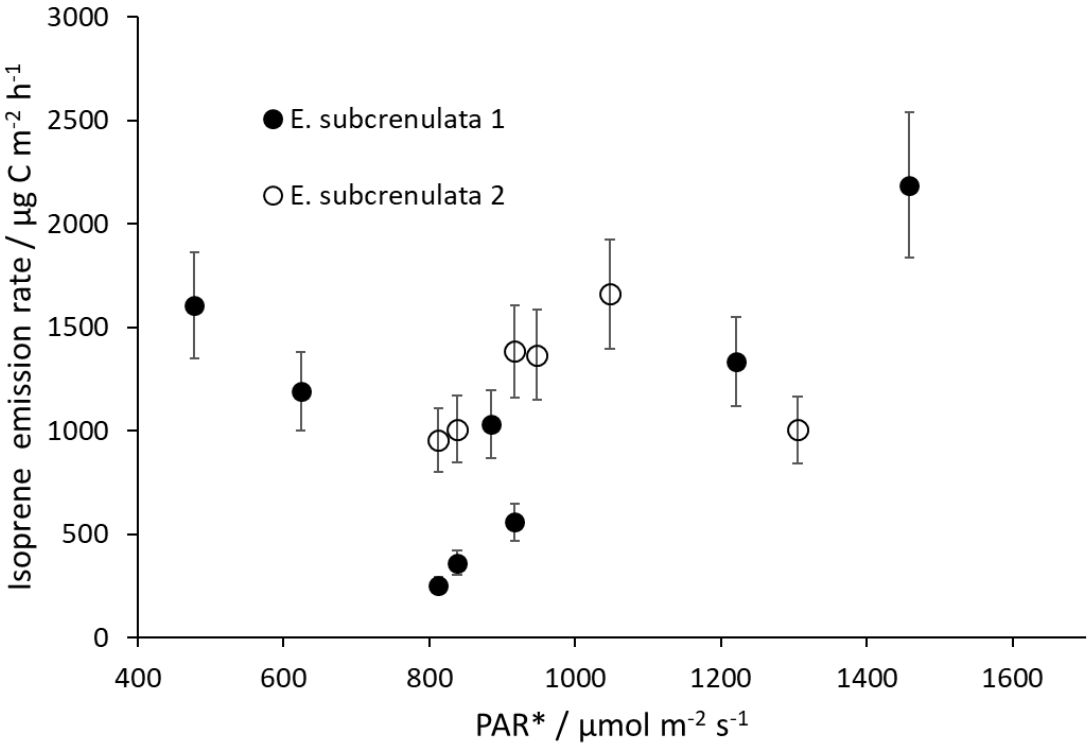
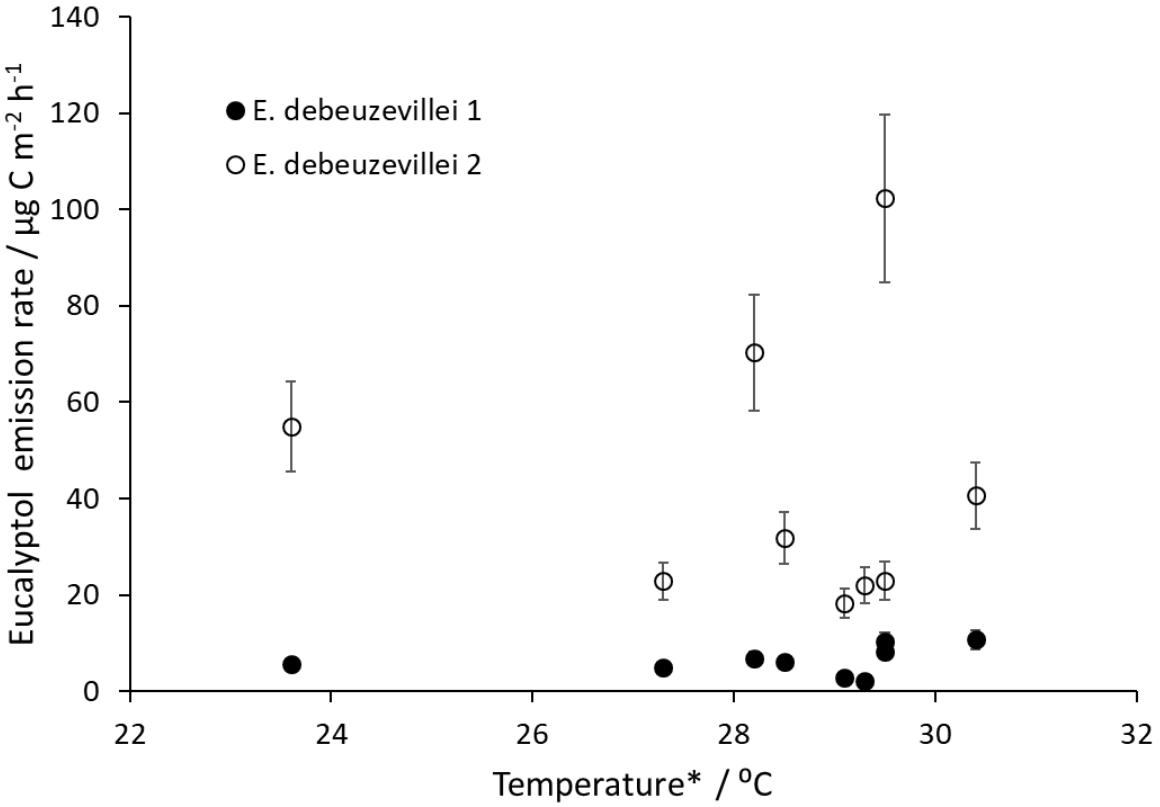


Figure 2 – Isoprene emission rate as a function of photosynthetic active radiation (PAR) for two individual trees of *E. subcrenulata*. *Represents average value recorded for PAR during each 30 min sample collection period.



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832 Figure 3 – Eucalyptol emission rates as a function of chamber temperature for two individual
833 trees of *E. debeuzevillei*. *Represents average value recorded for chamber temperature during
834 each 30 min sample collection period.

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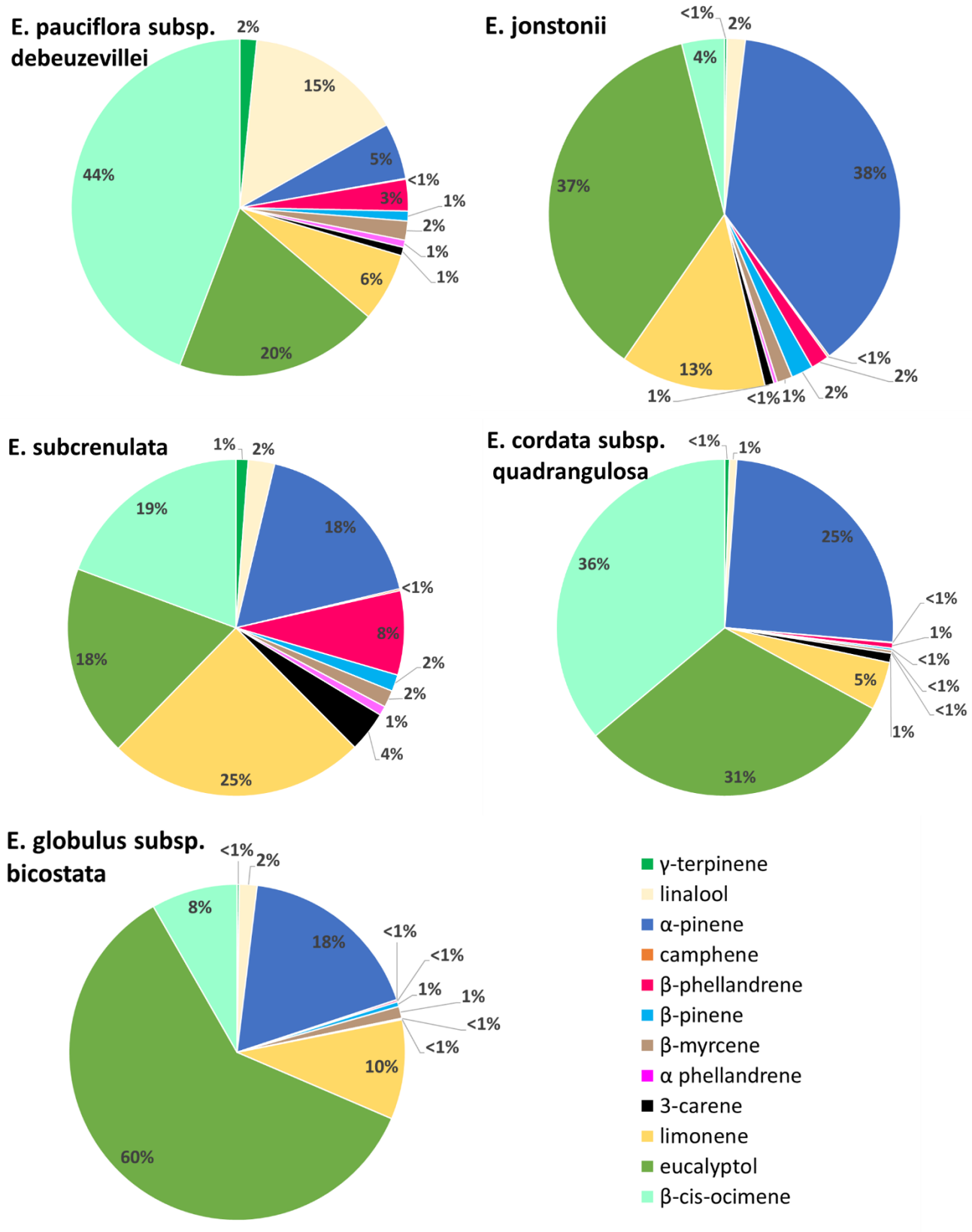

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841 Figure 4 – Average percentage contribution of individual monoterpenes relative to total
842 quantified monoterpene emissions.

Supplementary Information

Differences in isoprene and monoterpene emissions from cold-tolerant eucalypt species grown in the UK

Gemma Purser[*1,2], Mathew R. Heal[2], Stella White[1], James I.L. Morison[3], Julia Drewer[1]

[1] UK Centre for Ecology & Hydrology, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK

[2] School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh, EH9 3FJ, UK

[3] Forest Research, Alice Holt Lodge, Farnham, Surrey, GU10 4TT

*Corresponding author

Content

Table S1. Summary of the range of emission rates of isoprene and selected monoterpenes from single trees of eucalypt species grown and measured under a UK climate. N represents the number of samples measured and d is the number of days. The ranges in values of *T*, PAR and RH across the sampling occasions for each species are also presented.

Eucalypt species	*N*	d	*T* / °C	PAR / µmol m^{-2} s^{-1}	RH / %	Compound	Emission rate / µg C g_{dw}^{-1} h^{-1}					Emission rate / µg C m^{-2} h^{-1}				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
E. pauciflora subsp. pauciflora	9	2	21.9 – 30.5	411-1108	73.0 - 79.5	*isoprene*	2.03	1.38	0.58	4.61	1.61	325	220	75.2	704	296
						γ-terpinene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
						linalool	0.01	0.01	0.00	0.03	0.01	1.36	1.52	0.00	3.78	0.81
						α-pinene	0.05	0.05	0.00	0.17	0.03	7.74	9.98	0.00	30.7	4.24
						camphene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
						β-phellandrene	0.01	0.01	0.00	0.03	0.01	1.71	1.35	0.00	3.31	1.77
						β-pinene	0.00	0.00	0.00	0.01	0.00	0.40	0.45	0.00	1.41	0.28
						β-myrcene	0.01	0.01	0.00	0.04	0.01	1.62	1.81	0.26	5.10	0.81
						α-phellandrene	0.01	0.01	0.00	0.03	0.00	1.31	1.50	0.00	4.30	0.74
						3-carene	0.04	0.07	0.00	0.19	0.01	7.76	12.3	0.00	35.0	0.70
						d-limonene	0.05	0.06	0.00	0.18	0.03	8.43	8.75	0.00	22.6	4.43
						eucalyptol	0.04	0.05	0.00	0.15	0.02	5.96	8.74	0.16	27.9	2.77
						β-cis-ocimene	0.00	0.00	0.00	0.01	0.00	0.49	0.53	0.00	1.32	0.20
						Total MT	0.23	0.20	0.05	0.64	0.20	36.8	34.8	7.16	117	30.6

N = Number of measurements; T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard deviation

(Table S1 continued)

Eucalypt species	*N*	d	*T* / °C	PAR / µmol m^{-2} s^{-1}	RH / %	Compound	Emission rate / µg C g_{dw}^{-1} h^{-1}					Emission rate / µg C m^{-2} h^{-1}				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
E. gunnii subsp. gunnii	12	4	21.9 – 35.4	267 – 1108	73.0 – 86.7	*isoprene*	6.04	5.44	0.76	18.2	5.53	933	844	123	2790	6.04
						γ-terpinene	0.01	0.01	0.00	0.04	0.01	2.01	2.03	0.00	6.00	1.75
						linalool	0.04	0.06	0.00	0.16	0.01	6.40	8.97	0.00	24.3	1.63
						α-pinene	0.21	0.15	0.00	0.51	0.19	31.4	24.7	0.00	84.3	28.6
						camphene	0.00	0.00	0.00	0.01	0.00	0.41	0.72	0.00	1.74	0.00
						β-phellandrene	0.08	0.07	0.00	0.22	0.05	11.8	10.4	0.00	33.8	7.58
						β-pinene	0.02	0.01	0.00	0.03	0.02	3.01	1.64	0.00	5.12	3.56
						β-myrcene	0.08	0.08	0.00	0.23	0.05	11.4	12.1	0.00	35.3	6.68
						α-phellandrene	0.03	0.02	0.00	0.07	0.03	4.75	3.29	0.00	10.4	4.74
						3-carene	0.02	0.02	0.00	0.04	0.01	2.27	2.37	0.00	6.19	1.11
						d-limonene	0.14	0.12	0.00	0.39	0.11	21.3	18.6	0.00	59.5	15.7
						eucalyptol	0.11	0.12	0.00	0.36	0.07	16.7	18.3	0.00	55.5	10.4
						β-cis-ocimene	1.13	1.78	0.00	5.01	0.43	158	235	0.00	665	66.4
						Total MT	1.87	1.87	0.00	5.73	1.07	269	246	0.73	761	167

N = Number of measurements; T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard deviation

(Table S1 continued)

Eucalypt species	*N*	*d*	*T* / °C	PAR / µmol m^{-2} s^{-1}	RH / %	Compound	Emission rate / µg C g_{dw}^{-1} h^{-1}					Emission rate / µg C m^{-2} h^{-1}				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
E. gunnii subsp. divaricata	9	3	27.3 – 30.5	267 – 1323	75.1 – 86.7	*isoprene*	10.5	2.32	6.04	13.2	10.6	1650	375	1050	2300	1680
						γ-terpinene	0.00	0.00	0.00	0.01	0.00	0.31	0.51	0.00	1.43	0.10
						linalool	0.01	0.01	0.00	0.03	0.00	1.23	1.87	0.00	4.07	0.00
						α-pinene	0.06	0.04	0.02	0.12	0.04	10.1	7.49	3.56	21.1	5.74
						camphene	0.00	0.00	0.00	0.00	0.00	0.06	0.07	0.00	0.18	0.06
						β-phellandrene	0.01	0.00	0.01	0.01	0.01	1.39	0.40	0.89	2.16	1.53
						β-pinene	0.01	0.01	0.00	0.02	0.00	1.13	0.94	0.31	2.63	0.57
						β-myrcene	0.00	0.00	0.00	0.01	0.00	0.65	0.43	0.17	1.33	0.51
						α-phellandrene	0.00	0.00	0.00	0.01	0.00	0.43	0.45	0.00	1.09	0.28
						3-carene	0.00	0.00	0.00	0.02	0.01	1.61	0.92	0.70	3.75	1.46
						d-limonene	0.04	0.03	0.01	0.10	0.02	6.46	5.11	1.99	17.4	3.85
						eucalyptol	0.02	0.02	0.00	0.05	0.02	2.51	2.55	0.00	7.93	2.31
						β-cis-ocimene	0.02	0.01	0.00	0.03	0.02	2.15	1.78	0.00	4.90	2.54
						Total MT	0.18	0.05	0.08	0.25	0.17	28.0	9.46	13.1	42.8	24.9

N = Number of measurements; T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard deviation

907

908 (Table S1 continued)

909

Eucalypt species	N	d	T / °C	PAR / µmol m^{-2} s^{-1}	RH / %	Compound	Emission rate / µg C g_{dw}^{-1} h^{-1}					Emission rate / µg C m^{-2} h^{-1}				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
E. coccifera	10	5	18.1 – 31.8	324 - 1719	65.5 - 90.4	*isoprene*	2.11	3.27	0.01	9.53	0.32	453	723	1.21	2050	58.8
						γ-terpinene	0.02	0.04	0.00	0.15	0.00	3.36	9.94	0.00	34.7	0.05
						linalool	0.01	0.02	0.00	0.08	0.00	1.71	5.24	0.00	18.3	0.02
						α-pinene	0.13	0.21	0.00	0.73	0.05	28.7	47.9	0.00	163	9.99
						camphene	0.00	0.00	0.00	0.00	0.00	0.20	0.33	0.00	0.96	0.00
						β-phellandrene	0.11	0.24	0.00	0.84	0.01	23.8	54.0	0.00	187	1.34
						β-pinene	0.02	0.04	0.00	0.13	0.01	4.44	8.48	0.00	29.4	1.56
						β-myrcene	0.02	0.04	0.00	0.13	0.00	3.69	8.28	0.00	29.0	0.28
						α-phellandrene	0.00	0.00	0.00	0.01	0.00	0.39	0.90	0.00	2.40	0.00
						3-carene	0.01	0.02	0.00	0.08	0.00	2.72	5.23	0.00	17.0	0.00
						d-limonene	0.11	0.15	0.00	0.38	0.03	21.9	32.5	0.00	84.2	5.25
						eucalyptol	0.03	0.06	0.00	0.17	0.00	7.41	13.7	0.00	37.6	0.00
						β-cis-ocimene	0.12	0.32	0.00	1.12	0.00	26.9	72.5	0.00	252	0.84
						Total MT	0.58	1.09	0.00	3.77	0.11	125	247	0.00	848	20.6

910

911 N = Number of measurements; T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard deviation

912

913

914 Table S2 - Number of sampling days per month, average number of leaves measured, leaf
915 dry mass and leaf area for 9 species of eucalypt measured during this study.

	Number of sample days			*Average*		
Species	*June*	*July*	*August*	*number of leaves*	*Leaf mass (dry weight) / g*	*Leaf area / m^2*
E. coccifera	1	1	4	38	3.4	0.018
E. cordata subsp. quadrangulosa	1	1	2	22	5.5	0.032
E. globulus subsp. Bicostata	1	0	3	18	2.9	0.043
E. gunnii subsp. Divaricata	1	0	2	46	4.1	0.026
E. gunnii subsp. Gunnii	1	1	2	38	3.6	0.024
E. johnstonii	1	0	3	27	3.9	0.023
E. pauciflora subsp. pauciflora	1	0	1	11	6.4	0.041
E. pauciflora subsp. Debeuzevillei	1	1	3	11	3.8	0.025
E. Subcrenulata	0	1	3	23	3.6	*0.022*

916

917 Table S3 – Ambient air temperature and concentrations of ozone from the long-term
918 monitoring station (Bush cabin) at the UK Centre for Ecology & Hydrology, Penicuik,
919 Edinburgh on the days that VOC were sampled from 9 different species of eucalypt.

920

Sampling date	Air temperature / ^oC	Average ozone / $\mu g\ m^{-3}$
19/06/2019	18.0	No data
28/06/2019	20.9	No data
14/07/2019	No data	60.2
25/07/2019	26.6	117
13/08/2019	15.6	70.6
15/08/2019	17.1	70.9
23/08/2019	20.8	47.6
24/08/2019	25.1	93.7
25/08/2019	25.6	82.2
26/08/2019	22.1	67.7

921

922 DEFRA Air information resource https://uk-air.defra.gov.uk/data/

923 Accessed 28/5/2020

924

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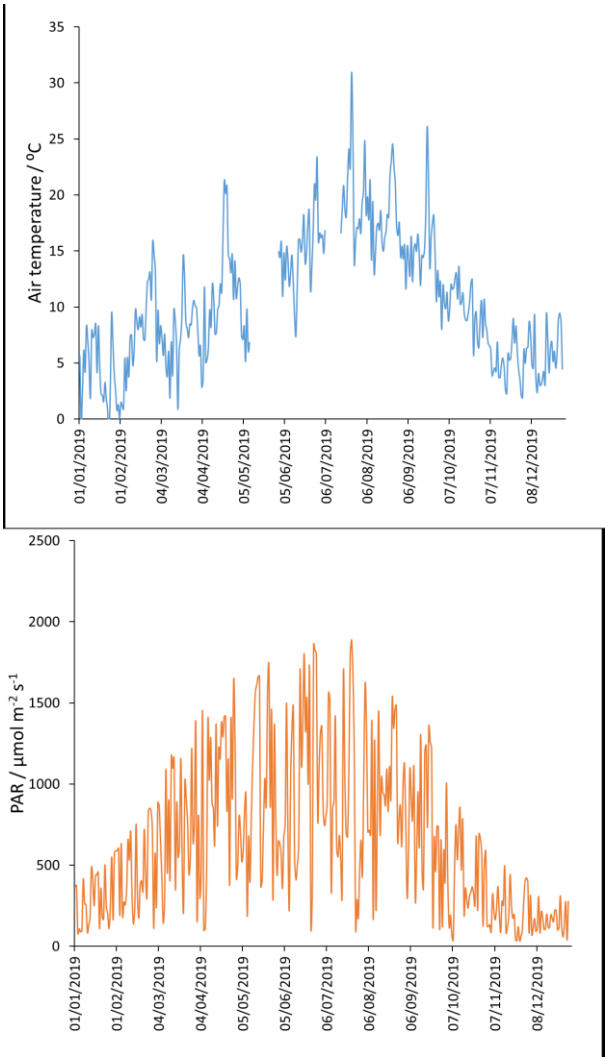

928

929 Figure S1 – Daily midday (12:00) measurements of air temperature and photosynthetic
930 active radiation (PAR) for January to December 2019, recorded at the UK Centre for Ecology
931 & Hydrology, Penicuik, Easter Bush.

932

933

934 Section S1

935 Several sources of uncertainties may influence the final emission rate for a given time point
936 and include the uncertainties on the following: ambient and chamber samples measured on
937 the GC-MS instrument; sample time; sample pump volume; chamber flow rate; leaf mass or
938 leaf area; chamber temperature; PAR measurement.

939 Given that net emission rates are derived from the difference between ambient and sample
940 measurements collected in parallel then some factors cancel out such as the error of the
941 certified standards, dilution of the certified standards (for monoterpenes) and the integration
942 of the peaks in the chromatogram. Given this, the uncertainty in an individual concentration
943 can therefore be determined by the interpolations for a given calibration regression fit.
944 Therefore the standard error in the interpolated concentration was determined using
945 Equation 1.

946

Equation 1

$$S_{x0} = \frac{S_{y/x}}{b}\sqrt{1 + \left(\frac{1}{n}\right) + \frac{(y_0 - \bar{y})^2}{b^2 \sum_i (x_i - \bar{x})^2}}$$

Sx_0 is the standard error in the interpolated concentration. $S_{y/x}$ is the standard error in the regression line and b is the slope of the regression line calculated using the regression function in Excel. n is the number of standards in the calibration line including the blank, which in this instance is equal to 5. y_0 is the experimental value of y which is the peak area of the compound measured in the chromatogram, $\bar{y}$ Is the mean peak area, x_i is the a standard concentration and $\bar{x}$ is the mean standard concentration.

The standard error in the interpolated concentration, $S_{\Delta c}$, was calculated for both the ambient sample $S_{ambient}$ and chamber sample $S_{chamber}$ was then calculated using Equation 2.

Equation 2

$$S_{\Delta c} = \sqrt{S_{chamber}^2 + S_{ambient}^2}$$

The final error propagation, $S_{measurement}$, (µg g_{dw}^{-1} h^{-1}) for an individual emission measurement, $ER_{measurement}$, (µg g_{dw}^{-1} h^{-1}) is then be calculated using Equation 3.

Equation 3

$$S_{measurement} = ER_{measurement} \times \sqrt{\left(\frac{S\Delta c}{\Delta c}\right)^2 + \left(\frac{St}{t}\right)^2 + \left(\frac{Shp}{hp}\right)^2 + \left(\frac{Sleaf}{leaf}\right)^2 + \left(\frac{SFlow}{Flow}\right)^2 + \left(\frac{ST}{T}\right)^2 + \left(\frac{SL}{L}\right)^2 + \left(\frac{SV}{V}\right)^2}$$

S_t is the error in the sampling time, t, estimated to be 30 seconds (0.01 h) for a 30 minute (0.5 h) sample time.

S_{hp} is the error in the hand held sampling pump (210-1003MTX, SKC ltd, Blandford Forum, UK) flow rate, hp, where the manufacturer quotes an uncertainty of 5%. S_{hp} is therefore 0.01 L min^{-1} for a flow rate 0.2 L min^{-1}.

S_{leaf} is the error in estimating the dry leaf weight, $leaf$, using the balance or leaf area using the Licor LI-3100C leaf area scanner. The errors quoted by the instrument manufacturers are 1% and 6% respectively, and so we attributed 6% to this measurement. S_{leaf} would be 0.24 g for a sample weight of 4 g and 0.024 m^2 for a leaf area of 0.4 m^2.

S_{Flow} is the uncertainty in the flow rate, $Flow$, of the chamber determined by the uncertainty as measured by the rotameter (Colepalmer, St. Neots, UK) given by the manufacturer to be 5%. For the flow rate 120 L h^{-1} (2 L min^{-1}) the S_{Flow} would be 6 L h^{-1}.

S_T is the uncertainty in the temperature, T, for the sample probe CS215 (Campbell scientific, Shepshed, UK) was estimated to be 4%. For a temperature of 30 ºC this would be 1.2 ºC.

S_L is the uncertainty in the measurement of PAR, L, using the SKP 215 PAR Quantum Sensor (Skye instruments, Llandrindod Wells, UK) which was suggested to be between 3-5%. For 5% this would be 50 µmol m^{-2} s^{-1} for a measurement of 1000 µmol m^{-2} s^{-1}.

S_V is the uncertainty in the chamber volume estimated to be 1% of the total volume, V. This would be 0.06 L for the 6 L chamber.